LEVEL II

SUMMARY

ANNUAL REPORT

QUANTUM CHEMICAL INVESTIGATIONS OF THE MECHANISM OF

CATIONIC POLYMERIZATION

Joyce J. Kaufman, Principal Investigator
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Baltimore, Maryland 21218

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20.

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II. Development of theoretical procedures for prediction of crystal structures and densities. (commenced April 1, 1980)

I. In the research on part I of this project we are carrying out ab-initio quantum chemical calculations and generating electrostatic molecular potential maps for cationic polymerization: on energetic monomers, on their interaction with catalysts and on the attack of the monomer-catalyst complexes on the substrates. This research is in support of an ongoing overall project of the Power Program Branch of ONR designed to develop energetic binders for use with energetic propellants. The propensity of polymerization of more conventional cyclic ethers had been shown experimentally to be proportional to their basicity and ring strain. We derived a theoretical index which should be proportional to the basicity of the monomers: namely, from the ab-initio quantum chemical calculations on the monomers generating the electrostatic molecular potential maps in space around the monomer. The more negative the map contours the farther out in space, the more basic should be the monomer.

The ab-initio calculations were calculated with our own programs which also incorporate several desirable options for calculations on large molecules and the maps were generated from these ab-initio wave functions.

The electrostatic molecular potential contour maps generated around the exotically substituted cyclic ether monomers proved to indicate correctly their different propensities for polymerization when the monomers were subsequently synthesized and polymerized experimentally by the other researchers on this overall ONR project. These electrostatic molecular potential contour maps can also shed insight on the question raised as to good copolymer candidates.

We have also carried out some necessary program development activities in connection with this research in improving convergence stability of our current ab-initio programs since this is sometimes a problem for nitro, fluoro and azido substituents and implementing new approaches to forming and solving SCF equations for reasonably large and closely related molecules or molecular systems.

II. We are pursuing several approaches to the prediction of crystal structures and densities. The first is to calculate (from calculations on the super-molecules) the SCF intermolecular interaction, separate it into its various components and use these to construct the crystal structure.

The second approach is to carry over the concept recently used successfully in calculations for biological systems where the same ab-initio calculations between two or several of such molecules for a large variety of inter-molecular configurations is used to derive atom class-atom class pair-pair and three-body potentials which are then used to calculate the intermolecular structure of an arrangement of molecules.

QUANTUM CHEMICAL INVESTIGATIONS OF THE MECHANISM OF

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QUANTUM CHEMICAL INVESTIGATIONS OF THE MECHANISMS OF

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SUMMARY

I. Ab-initio quantum chemical investigations of the mechanism of
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I.   In the research on Part I of this project we are carrying out ab-initio
quantum chemical calculations and generating electrostatic molecular
potential maps for cationic polymerization: on energetic monomers, on
their interaction with catalysts and on the attack of the monomer-catalyst
complexes on the substrates. This research is in support of an ongoing
overall project of the Power Program Branch of ONR designed to develop
energetic binders for use with energetic propellants. A binder which
itself was energetic would contribute significantly to the propellant
effectivity/weight ratio. The compounds of choice were cyclic ethers
(preferably 3- and 4- membered rings) substituted with exotic energetic
substituents such as fluoro-, nitro-, azido-, azidomethyl-, etc., either
singly or multiply substituted. The primary initial question asked was
could one predict the relative propensities of cationic polymerization
for these exotic monomers -- even before the monomers were synthesized.
The only previous old experimental Japanese paper reported that for cyclic
ethers substituted with more conventional substituents (alkyl-, alkoxy-,
aryl-) the rate of polymerization was proportional to the basicities
of the monomers and the ring strain. We derived a theoretical index which
should be proportional to the basicity of the monomers: namely, from the
ab-initio quantum chemical calculations on the monomers generating the
electrostatic molecular potential maps in space around the monomer. The
more negative the map contours the farther out in space, the more basic
should be the monomer.

The ab-initio calculations were calculated with our own programs
which also incorporate several desirable options for calculations on
large molecules: ab-initio effective core model potentials (MODPOT) which
enable calculations of the valence electrons only explicitly, yet

accurately; an integral prescreening evaluation (which we named VRDDO --
variable retention of diatomic differential overlap) especially effective
for spatially extended systems;and a MERGE technique which allows efficient
reuse of integrals from common skeletal fragments. These electrostatic
molecular potential contour maps were generated around the exotically
substituted monomers and some of the more conventionally substituted mon-
omers which had earlier been studied experimentally.

The electrostatic molecular potential contour maps generated around
the exotically substituted cyclic ether monomers proved to indicate correctly
their different propensities for polymerization when the monomers were
subsequently synthesized and polymerized experimentally by the other
researchers on this overall ONR project. These electrostatic molecular
potential contour maps can also shed insight on the question raised as to
good copolymer candidates. Since the rates of polymerization are governed
by basicity which in turn are predictable from these maps, the more
closely these maps match for two different monomers, the more well suited
these two monomers are for copolymer partners.

We have also carried out some necessary program development activities
in connection with this research. These have encompassed two areas:
improving the convergence stability of our current ab-initio MODPOT/VRDDO/MERGE
program systems, since convergence stability can sometimes be a problem
particularly for non-equilibrium orientations of molecules containing
fluoro, nitro, or azido groups, and implementing new approaches to forming
and solving SCF equations for reasonably large and closely related molecules
or molecular systems.

See next page for summary of Part II.

II. The arrangement of molecules in crystals is important in understanding intermolecular interactions which occur in crystals during detonation phenomena. Crystals densities are one of the important factors influencing detonation pressure and detonation velocity. Crystal structures and crystal densities can be calculated by ab-initio MODPOT/VRDDO/MERGE SCF supermolecule calculations, supplemented by an estimate of the dispersion energies (which are known to be much smaller than the other terms for nitro compounds). However, it would be most desirable to be able to calculate crystal structures and crystals densities by a intermolecular perturbation technique.

We are pursuing several approaches. The first approach is to calculate the SCF intermolecular interaction between two or several such molecules, then to separate this interaction into its electrostatic, polarization, exchange and charge-transfer components and then to use these components (with an estimate of the dispersion energy) to construct the crystal structure. We have done the analysis for this approach and are implementing it.

The second approach which we have just initiated is to carry over the concept recently used successfully in calculations for biological systems where the same ab-initio calculations between two or several of such molecules for a large variety of intermolecular configurations is used to derive atom class-atom class pair-pair and three-body potentials which are then used to calculate the intermolecular structure of an arrangement of molecules.

I. Ab-Initio Quantum Calculations and Electrostatic Molecular Potential
    Maps For the Mechanism of Cationic Polymerization

By making energetic binders for propellants, the efficiency/weight
ratio of propellants could be increased significantly.

ONR Power Program Branch is sponsoring an overall effort in this area
which combines other groups in experimental synthesis and polymerization
with our theoretical group. The objective of the ONR project is to prepare
energetic monomers of cyclic ethers (of ring sizes three-to-five-membered)
substituted with energetic groups (such as nitro-, fluoro-, azido-,
azidomethyl-) both single substituents and mixed substituents. We were
asked by ONR what insight quantum chemical calculations could shed on

1) the question of the propensity of the cyclic ethers with
   energetic substituents to undergo cationic polymerization prior
   even to synthesis of the energetic monomers themselves;
2) what happens as a catalyst (a Lewis acid) approaches the cyclic
   ether monomer and what might be preferable catalysts;
3) what happens as a complex of cyclic ether + catalyst approaches
   another molecule of cyclic ether monomer;
4) what would be good partners for co-polymerization in the event
   the polymer from a single monomer was too refractory -- too
   brittle.

It had been observed by Japanese investigators (Aoki, et al.), who
earlier studied experimentally three-to-six membered cyclic ethers with
more conventional substituents (alkyl, alkoxy, aryl) that the rate of
polymerization of cyclic ethers was proportional to

a) the base strength of the cyclic ether
b) the ring strain of the cyclic ether.

Thus, to determine propensity for polymerization, we had to come up
with theoretical quantum chemical indices that would be predictive of
basicity and of ring strain. Our previous ab-initio quantum chemical
calculations on morphine (an N-methyl narcotic agonist) and on nalorphine
(an N-allyl narcotic agonist-antagonist) had shown that charge alone on an
atom does not seem to be sufficiently sensitive to distinguish different
degrees of basicity especially for closely related molecules. However,
the use of electrostatic molecular potential contour maps did hold promise
of being a sensitive criterion for basicity. Comparisons of negative
regions of the maps around the O atom in the cyclic ether ring (both
spatial extent and magnitude) should be indicative of the relative basicities
of these exotic monomers. For the cyclic ether monomers, we reasoned
that the larger in space the negative contours of the map around the oxygen
atom in three dimensions, the more basic the monomer would be and the
more prone to cationic polymerization. For each monomer we are carrying
out the ab-initio calculations to optimize the geometry of the monomer.
As the geometry is optimized we then generate electrostatic molecular
potential contour maps in three dimensions around the monomer from the

calculated electronic wave functions of the monomer. These maps indicate vividly the basicity of the oxygen, from which direction a cation will prefer to attack the monomer and are especially valuable in comparing three dimensional relative basicities of various monomers. These maps have been generated around a number of the monomers and around some monomer-catalyst complexes.

We are carrying out ab-initio MODPOT/VRDDO and ab-initio MODPOT/VRDDO/MERGE calculations for 3-, 4-, 5- and 6-member cyclic ethers with various substituents. The 3- and 4-member rings are the ones of choice for the experimental program. In particular, the four member rings 3,3-fluoronitrooxetane and 3,3-dinitrooxetane were of the first interest experimentally. We carried out ab-initio MODPOT/VRDDO/MERGE calculations on oxetane and on the 3,3-fluoronitrooxetane and 3,3-dinitrooxetane and generated electrostatic molecular potential maps around the molecules in three directions i) parallel to the mean molecular plane (xz); ii) parallel to the (xy) plane and iii) parallel to the (yz) plane. The results for

      (a) Oxetane (Figures 1a and 1b)
      (b) 3,3-Fluoronitrooxetane (Figures 2a and 2b)
      (c) 3,3-Dinitrooxetane (Figures 3a and 3b)

indicate quite clearly that oxetane is the most basic, 3,3-fluoronitrooxetane is next and 3,3-dinitrooxetane is the least basic. The ring strains are not expected to differ nearly as drastically in these molecules as do the basicities. The maps suggested that the 3,3-dinitrooxetane should be so weakly basic that it would have trouble undergoing cationic polymerization. Very recent experimental data which indicates it appears to be very difficult to polymerize dinitrooxetane validates our hypothesis. Thus, it now seems possible that by carrying out the ab-initio quantum chemical calculations on these cyclic ether monomers with combinations of exotic energetic substituents even prior to the synthesis of the monomers themselves, we will be able to get considerable insight into the propensity of these monomers to undergo cationic polymerization. We are currently developing theoretical procedures for calculating relative ring strains in these cyclic ethers. Thus, in response to question 1), it would be expected that oxetane would polymerize more easily than fluoronitrooxetane and that more easily than dinitrooxetane.

These electrostatic molecular potential contour maps can also be used to help answer question 4) as to good candidate partners for copolymerization. We hypothesized that since the rate of polymerization is very dependent on the basicity of the cyclic ethers, for good copolymerization the copolymer molecules should have reasonably similar basicities (as well as ring strains), because if one compound was much more basic than the other, it would self-polymerize so fast that it would not have much tendency to copolymerize. 3,3-bis(azidomethyl)oxetane forms a polymer which is too refractory (too brittle). The question was asked as to possible good copolymer candidates for 3,3-bis(azidomethyl)oxetane. The maps showed that 3,3-bis(azidomethyl)oxetane was less basic than oxetane, more basic than 3,3-fluoronitrooxetane and apparently fairly similar in basicity to 3-azidooxetane. Thus, 3-azidooxetane might be a good choice for a copolymer candidate.

3,3-dinitrooxetane

Fig. 3a
Parallel to XZ plane
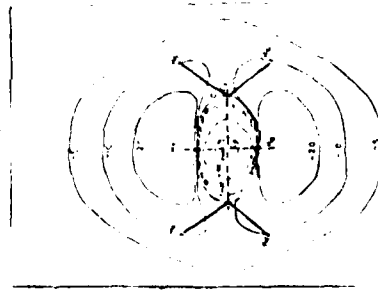y = 0.0 Å

Fig. 3b
Parallel to XY plane
z = -1.5 Å

3,3-fluoronitrooxetane

Fig. 2a
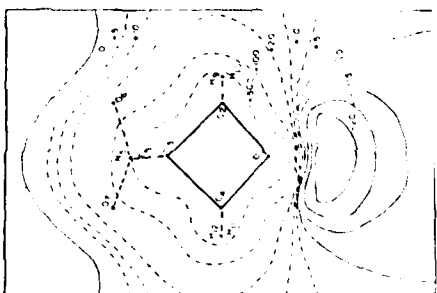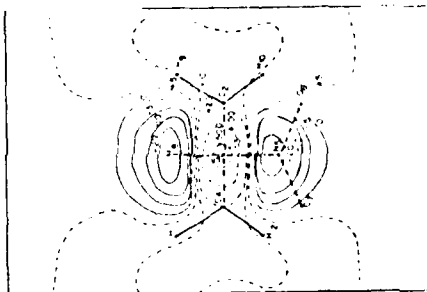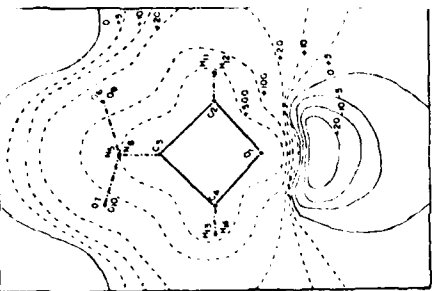Parallel to XZ plane
y = 0.0 Å

Fig. 2b
Parallel to XY plane
z = -1.5 Å

oxetane

Fig. 1a
Parallel to XZ plane
y = 0.0 Å

Fig. 1b
Parallel to XY plane
z = -1.5 Å
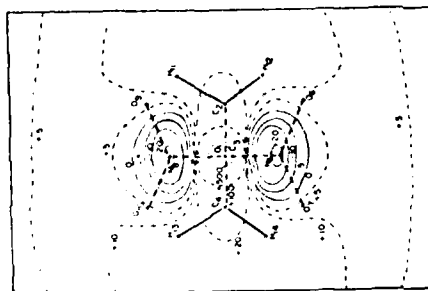
To shed insight on questions 2) and 3) we are also carrying out ab-initio MODPOT/VRDDO and ab-initio MODPOT/VRDDO/MERGE calculations on BF_3 approaching various series of substituted cyclic ethers and generating the electrostatic molecular potential contour maps. These results indicate the charge redistribution and changes in the maps as the reactants approach. Similar calculations are carried out for attack of H^+ on the substituted cyclic ethers since there has been speculation by experimental polymer chemists that perhaps it is the attack of H^+ (formed from a Lewis acid-H_2O complex) that triggers the polymerization. However, experimentally it has been observed that different Lewis acid catalysts have different effects on polymerization of the same monomer. For example, it is possible to polymerize certain of these energetic monomers with PF_5 but not with BF_3. This would seem to indicate that a catalyst-monomer complex might still be important. We suggested several experiments that could help clarify the picture. First, to measure the differing amounts of H^+ formed by various Lewis-acid catalysts in the polymerization solvent mixture (without any monomer as well as with monomers) to see if the amount of H^+ formed could explain the difference in propensity of a monomer to polymerize with different Lewis-acid catalysts. Second, to add various amounts of H^+ to solutions of monomer plus ineffective Lewis-acid catalyst to see if the extra H^+ could trigger the reaction. Third, to add various amounts of H^+ to solutions of monomer plus effective Lewis-acid catalysts to see if the rate or character of the polymerizations are affected.

Molecular Calculation Summary

The parent molecules studied so far have come from three sources:

- ONR molecules of interest

- Molecules from the Aoki, Harita et al. reaction rate study
  [J. Polymer Sci. Al $\underline{6}$, 2585 (1968)]

- A systematic study of single alpha substituents to round
  out and extend the Aoki et al. results.

These parent molecules are also being investigated in attack by a
proton and by boron trifluoride.

The following abbreviations are used in the table:

for origin: N   = ONR molecule of interest.

                 J   = Aoki et al. study.

                 S   = Systematic single α substituent study.

for status: O   = Geometry optimization completed.

                 A   = Geometry optimization approaching completion.

                 G   = Geometry optimization being done.

                 C   = Convergence difficulties encountered, but
stability problems are in the process of
being overcome.

              $I(x)$ = In plane proton attack (where the reacting
species approaches in the plane of the parent
that contains the hetero-oxygen and its ring
neighbors).
Geometry optimization completed. x is the
equilibrium H^+ - O distance.

            $IA(x)$ = Similar to $I(x)$ but geometry optimization
approaching completion.

            $PA(x)$ = Out of plane proton attack geometry optimization
x is the angle of optimal attack.

PARENT RING SYSTEM	MOLECULE	ORIGIN	PARENT MOLECULE	CALCULATIONAL STATUS		BF$_3$ ATTACK
	Oxirane	J,S	O	I(1.031Å)	PA(±46°)	G
	2-Methyloxirane	J,S	A			
	2-Ethyloxirane	J,S	G			
	2-Hydroxyoxirane	S	O			
	2,3-Bis(azidomethyl)oxirane	N	G			
	2-Azidomethyl)oxirane	N	G			
	2-(2,2-Dinitro-2-fluoroethoxy)oxirane	N	G			
	Oxetane	J,S	O	I(1.028Å)	PA(±10°)	G
	2-Methyloxetane	J,S	G			
	2-Ethyloxetane	S	G			
	2-Hydroxyoxetane	S	G			
	3-Azidooxetane	N	O	I(1.029Å)	PA(−15°)	G
	3,3-Bis(azidomethyl)oxetane	N	C,G	IA(1.035Å)		G
	3,3-Dinitrooxetane	N	O			
	3-Fluoro-3-nitrooxetane	N	G			
	Oxolane(THF)	J,S	O	I(1.017Å)	PA(5°)	G
	2-Methyloxolane	J,S	A			
	2-Ethyloxolane	S	G			
	2-Hydroxyoxolane	S	A			
	Oxane	J,S	O	IA(1.022Å)		G
	2-Methyloxane	J,S	A			
	2-Ethyloxane	S	G			
	2-Hydroxyoxane	S	G			
	4,7-bis(fluorodinitromethyl)-dioxepane	N	O			

Proton Attack Geometries:

Cα — O — Cα

O

H⁺

"TOP VIEW"

Cα   O ω   H⁺ — plane of the ring
O& the αC's

"SIDE VIEW"

Cα — (H)⁺ — Cα   OR   Cα — O — Cα
                          H⁺
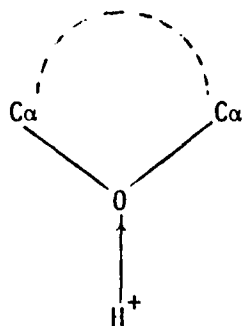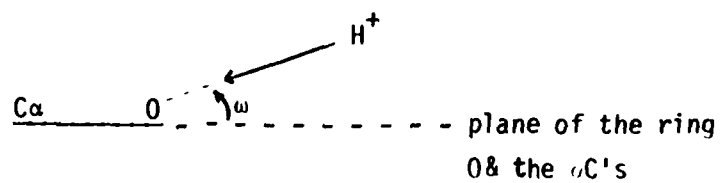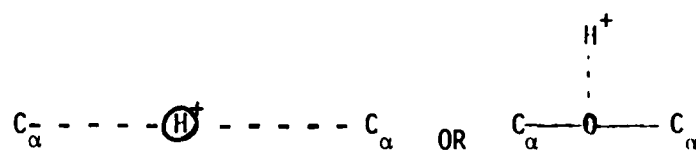
"FRONT VIEW"

Calculational Status

Electrostatic Molecular Potential Contour Maps Calculated

Oxirane with BF_3 distances of 1.0, 1.5, 2.0, 2.5, 5.0 Å

2-Hydroxyoxirane

Oxetane

3,3-Dinitrooxetane

3-Fluoro-3-Nitrooxetane

3-Azidooxetane

3-Azidooxetane with BF_3 B-O distances of 1.0, 2.0, 2.5, 5.0 Å

3,3-Bis(azidomethyl)oxetane

Oxolane (THF)

Oxolane with BF_3 B-O distance of 1.0 Å

Oxane

Oxane with BF_3 B-O distances of 1.5, 2.0, 5.0 Å

4,7-Bis(fluorodinitromethyl)dioxepane

We have also carried out some necessary program development activities in connection with this research. These have encompassed two areas.

We have improved the convergence stability of our ab-initio MODPOT/ VRDDO/MERGE program systems since SCF convergence stability can sometimes be a problem, particularly for non-equilibrium orientations of molecules containing fluoro, azido or nitro substituents. A simple, but elegant, attempt at stability control is to monitor the quality of the density matrix. Normally the reduced density matrix is computed as a sum over all occupied orbitals. In a destabilized iteration, a normally occupied orbital can become unoccupied. In our new approach, this orbital is not included in the density sum and the density is weighted to correct for its absence. This prevents the contamination of unoccupied orbitals and contributes to iterative stability. In essence, this is a ersatz projection technique and works well for these systems.

The improvement to traditional SCF methodology is based on the chemical knowledge that if one part of the environment of a reasonably large molecule changes, then radical restructuring of the electronic structure will most likely be confined to the locality of the change. This is reflected in changes to the coefficients of atomic basis functions in the vicinity of the site. We have formulated an exact, variational process for freezing in the molecular wave function the coefficients of some of the atomic basis functions (derived as a result of a previous molecular calculation) and iteratively computing the unfrozen "reactions" functions coefficients. In practice, however, one needs the entire set of coefficients unfrozen, so we have devised and implemented a revised SCF scheme whereby some coefficients are frozen, SCF convergence achieved for the unfrozen set, and then converging the entire unfrozen set. The potentialities for computational enhancement are great since the effective basis set size is reduced substantially during freezing. Consider a calculation of BF_3 attacking THF using a small basis of 4 functions per atom, except for hydrogen, which has one. Freezing all functions except those on oxygen, boron or fluorine leaves 20 unfrozen. The work to construct the Fock matrix to perform a diagonalization is proportional to the cube of the size, so by freezing we expect to perform only 9.4% of the work. If we additionally freeze the F basis functions, the work is now only 0.6% of the original! And we can unfreeze in stages. First keep unfrozen B and O. Then unfreeze F, and finally the whole system. This leads not only to speed enhancement but also to convergence stability. This technique will be particularly valuable as we sequentially bring catalyst up to monomer, then allow the monomer-catalyst to attach the substrate building up polymer chains.

II. Prediction of Crystal Structure

We are using two different approaches to tackle the problem of prediction of crystal structure.

In the first approach, while crystal structure predictions could be done by carrying out ab-initio SCF calculations of the entire super-molecule, it is more desirable to try to carry out such calculations in terms of the interactions between molecules and perturbation theory. For this purpose we need to be able to calculate separately the electro-static, exchange (repulsion), polarization and charge transfer energy contributions to intermolecular interactions (these come from proper partitioning of the SCF solution) and to estimate accurately the dispersion energies, and we are working on these aspects. In particular the polar-ization term must be modified to take neighbor effects into account. We are carrying out the preliminary analysis and are coding and putting together various program pieces necessary for this approach for ab-initio calculations for prediction of crystal structures.

Concomitantly, through the graciousness of Dr. P. Claverie (who spent time with us at Johns Hopkins twice last year), we are putting up on the computers we use a less rigorous program for analysis of crystal geometries and for intermolecular interaction energy. This was the method that had success in his previous analysis of the crystal structure of nitrobenzene. We shall explore the features of this method while we are writing our ab-initio method.

The second approach which we have just initiated is to carry over the concept used successfully recently in biological systems of carrying out ab-initio SCF calculations between several such molecules (in a variety of orientations), from these deriving ab-initio atom class-atom class pair-pair and three body potentials which can then be used to calculate intermolecular molecular structure accurately. We have examined these available biological ab-initio potentials and they lack the potentials for nitro, fluoro, azido and for aromatics and for aliphatic heterocyclics substituted with these. Thus we shall carry out the ab-initio inter-molecular calculations on such exotic species and derive the necessary potentials. A large number of such ab-initio calculations are necessary but we have the advantage of being able to use our ab-initio MODPOT/VRDDO/ MERGE technique, which saves considerable time. For example, for nitro-benzene which was our original test molecule the ab-initio calculation with the entire 6-3 G basis set took (on a CDC 6600 NOS/BE 1.3) 2691 seconds, the VRDDO calculation took 1000 secs., the MODPOT calculation took 717 secs., and the MODPOT/VRDDO calculation took only 321 secs. The savings in time with our method go up as n^x as the molecules get larger or as calculations are carried out on intermolecular systems (where $1 < x < 4$ depending on the size and shape of the molecule, since n^4 is the ultimate increase in the number of integrals with the number of atomic basis functions provided no integrals are small). Our previous extensive testing on a number of molecules had shown that the orbital energies and gross atomic populations for all four calculations agreed to almost 0.001-0.002 a.u. or e, and

potential energy curves agreed even better, to 0.001 - 0.0001 a.u. As an extra bonus, we showed last year that the MODPOT basis sets we use are so well balanced that there is very little superposition error when these are used in intermolecular calculations.

The derived atom class-atom pair potentials are then general for a particular substituent or skeleton. Thus, they can then be used to predict crystal structures of any energetic compound containing those structural subunits.

III. Joyce J. Kaufman - Invited Lectures Presented on this ONR Research

   A. Invited Lectures Presented at the Following National and
      International Meetings, Including Results on the Energetic Monomers.

March 1980. International Sanibel Symposium on Atomic, Molecular and
      Solid State Theory, Palm Coast, Florida.

March 1980. Symposium on Electrostatic Potentials in Chemistry, National
      American Chemical Society Meeting, Houston, Texas. In press in the
      Proceedings of the Meeting.

June 1, 1980. 7th Canadian Theoretical Chemistry Conference, Banff,
      Alberta.

July 1980. NATO Advanced Study Institute on Fast Reactions in Energetic
      Systems, Preveza Beach, Greece. Also presented tutorial lectures.
      In press in the Proceedings of the Meeting.

   B. Invited Lectures Presented at ONR or DOD Meetings.

August 1979. Quantum Chemical Calculations for Energetic Compounds
      (Explosives, Propellants, Etc.), Conference on Thermal Decomposition
      of Propellants and Explosives, Air Force Academy, Boulder, Colorado.

September 1979. Quantum Chemical Investigations on the Mechanisms of
      Cationic Polymerization and Cationic Graft Polymerization; Workshop
      on Energetic Binders, ONR, Washington, D.C.

April 1980. Ab-Initio Quantum Chemical Calculations and Electrostatic
      Molecular Potential Contour Maps Around Energetic Cyclic Ethers.
      ONR Contractors' Meeting, SRI, Palo Alto, California.

April 1980. Ab-Initio Quantum Chemical Techniques for Large Molecules
      and Application to Cationic Polymerization. Discussion of Navy
      research interests, Naval Research Laboratories.

   C. In addition, at the request of Dr. Richard Miller, our ONR
       contract monitor, we have made a number of trips to ONR and
       NRL to discuss various aspects of research.

IV. Project Personnel

Joyce J. Kaufman, Ph.D., Principal Investigator

Frank C. Tobin, Ph.D.
    The majority of the quantum chemical calculations and the new
SCF program development reported here are due to him.

P. C. Hariharan, Ph.D.
    Working part time with this project initially since he was already
familiar with our various computer programs necessary for the ab-initio
quantum chemical calculations and electrostatic molecular potential
contour maps and he has also made various addition to these programs
as needed for the present research. Now participating in the development
of the program for predicting crystal structure.

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